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(54) Title: LIGNIN-BASED VAPOR BARRIER FORMULATIONS

(57) Abstract

The invention provides for a vapor barrier formulation suitable for coating and lamination onto a paper substrate and comprises organosolv lignin in a dispersion, mica and latex. The laminated paper product is recyclable.

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LIGNIN-BASED VAPOR BARRIER FORMULATIONS

BACKGROUND OF THE INVENTION

Generally speaking, a water vapor barrier is one or more walls of multiwall shipping sack container or wrapper that by itself has a degree of resistance to the passage of water vapor from the surrounding atmosphere to the packaged product or that has been coated, impregnated or laminated with a material that gives it such resistance. A water vapor barrier is generally rated by its water vapor transmission rate (WVTR), WVTR is the rate of water vapor transmitted through a barrier at a given temperature and relative humidity. A water vapor barrier is generally used to protect a product with an affinity for moisture which could cause a physical or chemical change in the product rendering it unusable.

Paper is widely used in a variety of commercial and mechanical applications such as in the manufacture of flexible packaging, corrugated and solid fiber boards. The physical properties of paper and its relatively low cost are important considerations making paper attractive for a number of applications.

Certain properties of conventional paper have limited its use in many mechanical applications. For example, conventional paper readily absorbs moisture and has exceptionally poor wet strength. When conventional paper is placed in direct contact with water, or is

exposed to the weather, it readily absorbs ambient water and as a result exhibits essentially no wet strength. For many paper products, such exposure to moisture and resulting reduction in wet strength can destroy the product's usefulness. Another property of paper which makes it undesirable for certain applications is its absorption of oils and greases which makes it unsuitable for use in packaging of products containing oil or grease.

To expand the use of paper, paper has been treated, laminated, coated, or combined with other materials to form an impervious barrier to meet the requirements of a specific end use. The most common paper applications with barrier requirements are applications for multiwall shipping sacks, paper wrappers and food packaging call for resistance to water, moisture, grease, oils, gas, and odor.

Multiwall kraft paper when combined with one or more barrier materials with specific properties results in a balanced cost/performance ratio package. Coatings are usually extruded on multiwall kraft substrate in single, or multiple layers. Coatings and film embrace an ever increasing number of available polymers and modified polymers in addition to composite single films consisting of two or more layers of specific property resins. These structured films can be produced by extrusion or adhesive lamination or by coextrusion.

Shipping sac films are frequently referred to as free or unsupported films. In fabricated bags, however, they often appear as supported film. That is, they are attached by adhesion or heat lamination. By far, the highest volume growth of plastic coatings and film used in multiwall shipping sacks has been polyethylene, which can be made in a range of densities, with varying strength, flexibility, and melt temperature. Major contributing factors have been availability, low cost, and its performance as a water vapor barrier, which is the most common barrier requirements for shipping sacks.

Laminated paper is a generic term covering any combination of at least one ply of paper bonded to one or more piles of paper, plastic film, cellophane, foil, or other material. Thus, laminated paper would, for example, range from two plain sheets of kraft bounded together with starch adhesive, to a complex structure of kraft laminated to polyethylene/foil/polyethylene.

Foil/paper laminations consist of kraft bounded by an adhesive or laminating agent, usually wax, hot melt, or polyethylene extrusion, to a continuous sheet of metallic foil.

Greaseproof, along with glassine and vegetable parchment paper are barriers for product containing grease or oil. Greaseproof paper utilizes special sulphite or sulphate (kraft) pulps that are "hydrated." Glassine is made by running a greaseproof sheet through a series of

alternating fiber and steam heated steel rolls at high pressures and temperatures. In addition to its grease resistance, glassine has good machinability, an excellent printing surface, and can readily be combined with various films and foil to meet specific packaging requirements. Since wax laminate softens above 120°F, wax laminated glassine would be unsuitable for direct contact with very hot products in the packaging operation.

Sulphate or kraft wood pulp is now used instead of cotton fibers in vegetable parchment. Waterleaf paper, bleached, unsized, and free of other filling materials, is used as the base stock. The outstanding characteristics of vegetables parchment for packaging purposes are its combination of high greaseproofness and wet strength. Standard grades resist penetration of almost any type of oils, grease, turpentines etc., and retain a high percentage of strength when wet. Because of its inherent poor dry strength property, it is difficult to handle when covering equipment.

Roll wrap is commonly referred to as the paper used to wrap rolls to prevent them from re-adsorbing moisture and reverting in brightness. In roll wrap, the most common materials used as moisture vapor barrier are petroleum-based products such as polyethylene, polypropylene or wax. These products have excellent moisture vapor barrier properties, can be applied economically and have been widely used in the industry. Roll

wrap paper is typically made with two plies of liner board laminated together with wax or polyethylene.

While plastic films and roll wrap paper have good barrier properties, they are not recyclable into paper since the barrier material (polyethylene, polypropylene or wax) contaminates the final product and causes operational problems in screening and other paper making equipment. Therefore, roll wrap must be carefully removed from the paper recycling system and be land-filled after use. The cost to landfill is skyrocketing due to the ever shrinking availability of landfill sites.

As an alternative to land-filling, incineration and composting have found applicability with composting gaining popularity over incineration due in part to environmental concerns about incineration relating to atmospheric emissions and ash toxicity. Composting has been gaining in popularity provided the material to be composted has the adequate carbon to nitrogen ratio of 25 to 30 carbons for every nitrogen.

The recyclability of moisture vapor barrier wrappers has become a major concern as landfill space has become less available and the cost involved with recycling has become prohibitive. Therefore, there is a need to make mill wrap more compatible with the typical paper

recycling process by changing the moisture vapor barrier coating or laminate.

By the methods of the present invention is provided environmentally friendly lignin-based formulations suitable for lamination. The formulations are aqueous-based, meet vapor barrier specifications and performance requirements for packaging products, and promote recyclability in comparison to the current industry standard. Organosolv lignin with its hydrophobic nature is a good candidate for the formulations of this invention.

SUMMARY OF THE INVENTION

It is an object of this invention to provide for vapor barrier formulations. The formulations are comprised of an organosolv lignin, mica and latex. In one embodiment, the lignin can be comprised in an ammonia dispersion and in another embodiment, the lignin can be comprised in a polyacrylate dispersion. The formulations of this invention can be coated and laminated on a paper substrate to produce a paper laminate product which can be recycled.

Other features and aspects of the invention, as well as other benefits will be readily ascertained from the more detailed description of the preferred embodiments which follow.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The lignin employed in this invention is separated from plant biomass as a small biopolymer by a novel chemical delignification technology based on organic solvents, for example ethanol. Generally referred to as organosolv lignin, it is a free-flowing, nontoxic powder. It is soluble in aqueous alkali and in selected organic solvents. It is generally characterized by its hydrophobicity, high purity, melt flow and a low level of carbohydrates and inorganic contaminants.

The lignin of this invention can be formulated as an aqueous-based water vapor barrier for applications including, but not limited to roll wrap, roll headers, skid wraps, multiwall bags, cores, corrugated boxes and food packaging. Furthermore, the lignin formulations of this invention when laminated onto the appropriate paper substrate produce environmentally friendly end-products. The end-products can be recycled by repulping and leaving the lignin in the recycled paper. Alternatively the lignin may be removed by extraction from the laminate.

The lignin can be formulated as an aqueous dispersion using ammonia. The lignin dispersion is generally obtained by mixing lignin with an ammonia solution such that the final pH of the dispersion is of from about 8 to about 12. In order to reach the appropriate viscosity, the particle size of the lignin can be reduced to a final particle size of from about 0.1 micron to 20

microns, preferably of from about 0.5 micron to about 1.5 micron. The dispersion creates a self-dispersant for lignin and the ammonia is a fugitive cation which upon drying can be driven away leaving a hydrophobic lignin in the formulation. Alternatively, other dispersants or dispersant aids can be also used.

The lignin dispersion thus obtained can be mixed with a latex such as for example styrene-butadiene rubber, vinylidene chloride butadiene, neoprene or any other latex which is nonvolatile, non-migratory and can reduce the glass transition temperature of the lignin. If need be a filler can be added such as for example, mica which functions to stabilize the coating dispersion and is believed to be a water vapor barrier. The ratios are from about 40% to about 60% lignin, up to 33% mica and of from about 5% to about 35% latex on a dry weight basis. The lignin formulation thus obtained can be laminated onto a suitable paper substrate such as liner board or kraft paper.

In another embodiment, the lignin can be formulated as an aqueous dispersion using a dispersant which is stable in an acid system, such as polyacrylate. The lignin dispersion is generally obtained by mixing lignin with an aqueous solution of the dispersant such that the final pH of the dispersion is slightly basic to neutral. In order to reach the appropriate viscosity, the particle size of the lignin can be

reduced to a final particle size of from about 0.5 to about 5 micron.

The polyacrylate lignin dispersion thus obtained can be mixed with a latex such as for example, poly(vinyl) acetate or any other latex which is nonvolatile, non-migratory, has good adhesive properties and reduce the glass transition temperature of the lignin. If need be a filler can be added such as mica which functions to stabilize the coating dispersion and is believed to be a water vapor barrier enhancer. The ratios are of from about 5% to about 40% lignin, up to 20% mica and of from about 40% to about 60% latex on a dry weight basis.

The lignin formulations of this invention can be applied as a coating to a suitable paper substrate such as kraft paper or liner board. Any suitable technique such as a Meyer rod or a forward roll coater can be used. The coated substrates can then be laminated to a coat weight of from 40 to about 60 g/m^2. The type of latex used as a binder in the formulation will determine the lamination procedure to be used. Thus if the latex reduces the glass transition temperature of the lignin but has no cold adhesive properties, the coating will need to be dried and then laminated using heat and pressure. If the latex has good adhesive properties, the coating does not need to be dried to the same extent as in the previous case and the lamination will not require as much heat or pressure. The laminates of

this invention can provide for a WVTR of from about 4 to about 600 g/m^2/day.

The paper laminates of this invention can be recycled by slurrying them with an inorganic base such as for example, sodium hydroxide, ammonium hydroxide or a high alkali carbonate at a pH of from about 10 to about 12. The slurry is blended under typical pulping conditions such that the laminate breaks down into individual cellulose fibers and an alkaline lignin solution. The slurry is filtered on for example a drum filter or press filter to separate a solution of the lignin and a mat of fiber which is used to make paper. The filtrate can be acidified to a pH of from about 4 to about 6 to recover the lignin. Alternatively, the laminated product can be repulped under neutral conditions leaving the lignin on the fiber. Since this type of approach leads to somewhat speckled recycled paper, the fiber obtained is more compatible for use in the interior layers of a multiply paper product where the specs are not noticeable. By contrast, wax and polyethylene containing paper can not be used even as a filler fiber in the interior layers since they migrate or bleed to the surface of the paper in the dryer section of the paper machine causing operational problems. Therefore, wax or polyethylene laminates are currently land-filled or burned.

Example 1

A lignin dispersion was prepared by mixing 45% lignin in an ammonia solution such that the pH was 10. To reduce the particle size, the lignin dispersion was passed through a horizontal grinding mill from Premier Mill Corporation called the Supermill. The particle size was reduced from 10% below 1 micron to 87% less than 1 micron in diameter.

Example 2

The lignin dispersion of Example 1 was incorporated in a coating formulation as shown in Table 1.

Table 1

Component	(%) by weight
Lignin	27.45
Filler	14.10
Latex	8.30
Rheology Modifier	0.15
Water	50

The final Brookfield viscosity measured at 25°C and 100 rpm was about 2000 cps. The final solids content was about 50% and the pH was about 8.

Example 3

A lignin dispersion was prepared by mixing 45% lignin in a polyacrylate solution such that the pH was 6 to 7. To reduce the particle size, the lignin dispersion was treated as in Example 1.

Example 4

The lignin dispersion of Example 3 was incorporated as shown in Table 2.

Table 2

Component	(%) by weight
Lignin	20.30
Filler	8.70
Latex	28.71
Dispersant	0.29
Water	42.0

The final Brookfield viscosity measured at 25°C and 100 rpm was about 2500 cps. The final solids content was about 58% and the pH was about 6.5.

Example 5

The formulation of Example 2 was applied onto a base stock at a web speed of 30 M/min to

achieve a target moisture of 5% and a laminated coat weight of 44 to 54 g/m^2. Three different base stocks were coated: 26 lb liner board, 50 lb kraft sack and 60 lb freesheet web base stock. Results of WVTR measurements indicate an average WVTR of 7.3 g/m^2/day for a coat weight of 44.5 g/m^2 at a temperature of 25°C and 50% RH. Measurements were made on a MOCON Permatran-W 3/31.

Example 6

The formulation of Example 4 was applied onto a 78 lb liner board base stock at a web speed of 400 M/min to achieve a target laminated coat weight of 40 to 48 g/m^2 and a moisture content of 8 to 10%. Results of WVTR measurements indicate an average WVTR of 483 g/m^2/day for a coat weight of 43.9 g/m^2 at 40°C and 100% RH. Measurements were made on MOCON Permatran-W 3/31.

Example 7

Seven rolls were wrapped with the lignin coated wrapper of Example 6 along with seven control rolls with wax wrapper (2 turns wrap). No difference was noted on the wrapper station and the crimping station. A tight wrap was noted on the lignin wrapped rolls which is attributed to the slightly higher moisture content of the roll wrap.

The rolls were divided into two groups. One group of 8 rolls (4 wax + 4 lignin) was stored

at 25°C and 56% RH, and the other group was stored at 37°C and 40% RH to simulate hot temperature storage condition. Paper samples were taken from the roll 1/2 inch intervals to a depth of 2 1/2 inches. The samples were analyzed for any change in moisture and brightness for 32 storage days.

No significant difference in paper brightness and in moisture change for rolls wrapped with the wax coated wrapper or wrapped with organosolv lignin-based formulation. As shown in Table 3, the magnitude of the change is small and is considered within the normal variability of the coated paper or the measurement itself.

Table 3

	Brightness (ISO)	Moisture (%)
Wax Wrapper		
Initial	74.2	4.52
Final (25°C, 56% RH)	74.3	4.65
Final (37°C, 40% RH)	73.7	4.65
Lignin Wrapper		
Initial	74.1	4.41
Final (25°C, 56% RH)	74.0	4.6
Final (37°C, 40% RH)	73.9	4.6

Example 8

In this example, the laminates of Example 6 were recycled by repulping with water at a pH of 7.5 at 4.5% consistency and using a 200 HP pulper at higher speed.

The repulped lignin coated paper contained large flakes of dark color lignin coating. This furnish was used in a 50:50 ratio with old newspapers as the fiber for the middle plies (plies 2 through 5) in a six-ply chip board product. This was manufactured in a six cylinders Kobayashi Ultra-Former, 130" trim, 100 M/min to make a multipak chipboard of 720 g/m^2 basis weight, 5.5% moisture and 500 microns thickness. The chipboard obtained was of a quality as good as that of the product obtained when only old newspapers are used. There was no evidence of migration of lignin from the interior plies to the surface. No curling effect or other dimensional problems were observed.

In conclusion, the lignin coated paper has proven to be repulpable. If the presence of lignin specs is objectionable in the recycled paper, use of the lignin containing furnish can be limited to applications such as chipboard where it can be added in the middle plies to hide the presence of visible lignin specs.

This invention and many of its attendant advantages will be understood from the foregoing description, and it will be apparent that various

modifications and changes can be made without departing from the spirit and scope of the invention or sacrificing all of its material advantages, the specific materials, procedures and example hereinbefore described being merely preferred embodiments.

We claim:

1. A vapor barrier formulation suitable for lamination on a paper substrate comprising of from about 40% to about 60% organosolv lignin, up to 33% mica and of from about 5% to about 35% latex on a dry weight basis.

2. The formulation of claim 1 wherein said lignin is comprised in an ammonia dispersion.

3. The formulation of claim 2 wherein the particle size of said lignin is from about 0.1 to about 20 microns.

4. A vapor barrier formulation suitable for lamination on a paper substrate comprising of from about 5% to about 40% organosolv lignin, up to 33% mica and of from about 5% to about 35% latex on a dry weight basis.

5. The formulation of claim 4 wherein said lignin is comprised in a polyacrylate dispersion.

6. The formulation of claim 5 wherein the particle size of said lignin is from about 0.5 to about 5 microns.

7. A recyclable paper laminate comprising a paper substrate and a coating comprising a vapor barrier formulation comprising of from about 40% to about 60% organosolv lignin,

up to 33% mica and of from about 5% to about 35% latex on a dry weight basis.

8. The laminate of claim 7 wherein said lignin is comprised in an ammonia dispersion.

9. The laminate of claim 8 wherein the particle size of said lignin is from about 0.1 to about 20 microns.

10. A recyclable paper laminate comprising a paper substrate and a coating comprising a vapor barrier formulation comprising of from about 5% to about 40% organosolv lignin, up to 33% mica and of from about 5% to about 35% latex on a dry weight basis.

11. The laminate of claim 10 wherein said lignin is comprised in a polyacrylate dispersion.

12. The laminate of claim 11 wherein the particle size of said lignin is from about 0.5 to about 5 microns.

13. A method of making a paper laminate having vapor barrier properties, said method comprising the steps of:

combining in a formulation of from about 40% to about 60% organosolv lignin, up to 33% mica and of from about 5% to about 35% latex on a dry weight basis;

applying said formulation onto a paper substrate to produce a coating having a coat weight of from about 40 to about 60 g/m^2; and

laminating said coating.

14. The method of claim 13 wherein said lignin is comprised in an ammonia dispersion.

15. The method of claim 14 wherein the particle size of said lignin is from about 0.1 to about 20 microns.

16. A method of making a paper laminate having vapor barrier properties, said method comprising the steps of:

combining in a formulation of from about 5% to about 40% organosolv lignin, up to 33% mica and of from about 5% to about 35% latex on a dry weight basis;

applying said formulation onto a paper substrate to produce a coating having a coat weight of from about 40 to about 60 g/m^2; and

laminating said coating.

17. The method of claim 16 wherein said lignin is comprised in a polyacrylate dispersion.

18. The method of claim 17 wherein the particle size of said lignin is from about 0.5 to about 5 microns.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C09J 7/04; B05D 3/02; B32B 5/16, 29/00; C08L 97/00; C08K 3/34
US CL :156/327, 328; 427/391; 428/324, 325, 537.5; 524/72, 75, 76, 449
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 156/327, 328; 427/391; 428/324, 325, 537.5; 524/72, 75, 76, 449

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 2,558,634 (UBER) 26 JUNE 1951, see entire document.	1, 3, 4, 6
Y	US, A, 2,844,548 (HAXO ET AL.) 22 JULY 1958. See entire document.	1, 3, 4, 6
Y	US, A, 4,025,711 (DAVIDSON ET AL.) 25 MAY 1977. See entire document.	1, 3, 4, 6
Y	CA, A, 473,835 (POLYMER CORPORATION LIMITED) 22 MAY 1951. See entire document.	1, 3, 4, 6

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